

Tutorial 3.4 — Ion Exchange

Slide 1. Ion Exchange

This module will review the basics of ion exchange chromatography and some important chemical concepts that help to explain how ion exchange is used in radiochemical separations.

Slide 2. Learning Objectives

The learning objectives for this module are that the student will be able to:

- Discuss the chemical and physical properties of ion exchange resins used in radiochemical analyses.
- Describe how chemical equilibrium processes control analyte retention and elution.
- Describe the basic technique of ion exchange chromatography.
- Calculate the capacity of an ion exchange resin.

The key concepts that will be covered are:

- Anion exchange resins exchange anions.
- Cation exchange resins exchange cations.
- Any cation or anion can compete for active resin sites with ions of the same charge and the law of mass action may govern which ion is held most selectively.
- The general rules for selectivity of ions by a particular resin.
- The key factors in ensuring that effective ion exchange takes place during radiochemical separations.
- Every resin has a finite capacity based on its manufacture, and these capacities can be calculated and used to estimate the resins ability to selectively exchange ions.

Slide 3. What is Ion Exchange?

Ion exchange is an analytical chemistry separation technique that allows different ionic materials to be selectively retained on an ion exchange resin. An ion exchange resin is an ionic polymeric material that is insoluble in water, but has an exchangeable ion at several locations on the polymer chain called exchange sites. These exchange sites are made up of charged functional groups that are attached to the polymer. The functional groups generally used for resins in the analytical radiochemistry laboratory are sulfonic acids for cations and trialkylamines for anions.

Because the resins are insoluble in water, large volumes of sample can be passed over them and low concentrations of ions can be selectively removed concentrating the ions of interest on a much smaller volume of resin. In the process of concentrating one radionuclide of interest other ions and radionuclides that interfere with the analysis of the radionuclide of interest can be separated by selecting the appropriate solution chemistry conditions.

Slide 4. Structure of Ion Exchange Resins

Ion exchange resins are about 1–2 mm in diameter, amber to dark brown and very spherical. The characteristic of sphericity is important so that the resin bed spaces are uniform and no compaction of the beads takes place. Compaction would block flow prohibiting effective ion separation. The backbone of the resin molecule is a series of methylene groups with phenyl groups on alternate carbons. The phenyl groups have the functional group chemically bound in the 4 position. Physical strength is given to the resin by allowing cross-linking of the various

polymer chains. Laboratory resins have cross link values of about 6 to 8%. Commercial resins used for bulk water purification would have higher cross link values due to the hydraulic stresses put on these resins.

The figure on the slide shows the chemical structures of an anion exchange resin. Note that the functional group is a polyalkyl amine. The ionic portion of the resin that remains stationary is positively charged and the exchangeable ion is negatively charged- in this case a chloride ion.

The polymeric material that forms the resin creates channels inside the beads. These channels allow for the waters of hydration to become part of the bead structure. If we could look at the beads through a high powered microscope, we would see that these water filled channels allow diffusion of the ionic species to the inside of the bead where most of the beads functional exchange sites exist.

Slide 5. Resin Characteristics

In the previous slide we noted that water molecules hydrate the resin spheres. Even though a new ion exchange resin bead may feel dry to the touch it is actually approximately 50% by weight water. This water plays a critical role in the functioning of the resin. It allows ions to migrate through a continuity of water molecules so that exchange can take place with the functional groups inside the resin bead.

Resins should not be allowed to dry out in between uses. If they do dry out they will crack and break causing the spaces between the beads to become non-uniform. This non-uniformity in size creates blockage and channeling. Channeling limits the contact time between the eluent solution and the resin so that ion exchange does not occur as well. Channeling then leads to band spreading resulting in poor separation, or cross contamination of the eluted ionic species.

Slide 6. Anion Exchange versus Cation Exchange Resins

Ion exchange resins are classified as cation or anion resins.

An anion resin has a stationary, functional group with a positive charge. This means that it will exchange negative ions with the eluent solution. Anion resins are often shipped and stored in the chloride form because this maintains the long term stability of the resin.

A cation resin has a stationary, functional group with a negative charge. This means that it will exchange positive ions with the eluent solution. Cation resins are often shipped and stored in the sodium form, also to maintain their stability.

Slide 7. How Does Exchange Occur?

Ion exchange is an equilibrium process and has an equilibrium constant associated with it. The larger the size of the equilibrium constant the better retained the ion will be on a resin. The process of diffusion takes place as a result of a phenomenon known as chemical potential. That is ions migrate from a region of solution of high concentration to a region of solution of lower concentration. As the eluent with ions approaches a bead, the hydrated ion with its hydrated counter ion diffuse into the bead using the resins' water of hydration to migrate into the bead. When the appropriate ion approaches an exchange site, it replaces the resins labile ion which then diffuses back into the main flow of the eluent. The degree to which an ion is retained by the resin is known as the selectivity.

Selectivity is a parameter that is defined at specific solution conditions. Other equilibrium associated with the ion of interest may affect the selectivity of the ion. We will look at specific examples of this later on in this presentation.

Slide 8. Ionic Competition

The chemical equation shown on this slide identifies how a divalent cation would exchange on a resin. Note that two exchange sites are required to accommodate the calcium ion. All divalent ions would behave the same way. So, if we were attempting to use ion exchange to separate or concentrate radium ions from a drinking water sample, there would be competition for the available sites with calcium. For that matter, any cation (whether it is stable or radioactive) in solution will vie for those exchange sites. Thus solution conditions would need to be adjusted so that the exchange of the analyte of interest is most favorable.

Thus changing of the solution conditions after an ion has been exchanged onto a resin will change the equilibrium constant, and in many instances will allow the exchanged ion to elute.

Slide 9. Anion Exchange Selectivities

The table shown on this slide gives the relative order of ion selectivity for a strong base anion exchange resin. The higher the selectivity number the more tightly bound that ion is with respect to other ions of lower selectivity numbers. A general rule of selectivity is the higher the valence of the ion the more selective the resin is for that ion.

The solution pH can also have a profound effect on selectivity. High concentrations of H^+ ion or OH^- ion can cause the eluent to move the ions through the resin limiting their exchange.

Also note that the higher the charge density of the hydrated ion, the more selective the ion will be for the resin. Thus fluoride is the least selective anion and iodide the most selective.

Slide 10. Cation Exchange Selectivities

The table here shows the general selectivity for cations on a strong acid cation resin. The rules of selectivity are the same as for the anions. Selective elution will be more effective when the relative selectivity numbers are very different (like a factor of 2 or 3). Thus if you were to take a drinking water sample containing calcium and wanted to concentrate ^{90}Sr on a cation resin, would you be able to effectively selectively elute strontium from calcium? This discussion is continued later on in this module...

Slide 11. Test Yourself Exercise #1

The observed selectivity for the actinides is that tetravalent is the highest and pentavalent is the lowest. This is shown in the second sequence on the slide. Using some facts about the actinides in solution from the oxidation reduction module plus what you have just learned about ion exchange resins, verbally describe why the order is as observed. The discussion for this reason is on the next slide.

Slide 12. Test Yourself Exercise #1– Solution

Remember that ions that have valences of 5 or more form oxo-ions in solution. The +5 and +6 actinides form oxo-complexes in the ratio of 1 metal ion to two oxygen atoms. The resulting ions are positively charged, BUT they have two oxygen atoms each with two unshared, pairs of electrons. Those two oxygens give the ion a distinctive negative feature. Cation resins have a

sulfonic acid exchange group (a negative charge center). Thus when these oxo-ions approach an exchange site some electrostatic repulsion prevents a good selectivity.

Slide 13. Charge Density and Ion Exchange Selectivity

Charge density can be defined as the ionic charge divided by the volume of the hydrated ion. The example described on this slide is for the Group I periodic table cations. Although the actual ionic diameter of each ion increases as we increase atomic number, the number of water molecules that are attracted as the hydration sphere goes down as atomic number increases. This means that charge density increases with atomic number. Thus cesium is the most selective and lithium is the least selective of the metal ions.

Slide 14. Ion Exchange Chromatography

Generally the manner in which ion exchange separations are performed, are analogous to column chromatography. The resin is loaded into a column so that the height of resin is approximately 8 to 10 times the diameter of the column.

The resin should then be equilibrated with a solution isotonic to the sample load solution. The sample load solution should be as small a volume as is reasonable so that the sample will be quickly added onto the column. After the column equilibration is performed the sample solution is loaded onto the column. Solution chemistry conditions should have ensured that the analyte is selectively exchanged and should be in the top 2 or 3 cm of the resin.

The sample solution is allowed to drop just below the top level of the resin, and an isotonic rinse solution is put through the column.

Slide 15. Ion Exchange Chromatography (Part 2)

Once the ion exchange resin has been rinsed to remove general contaminants, the next process is elution of the radionuclides of interest. This may occur by either stepwise change in concentration or by a gradient (slow change) in concentration using eluent of different chemical constituency so that one retained material is eluted at a time. Once the radionuclide of interest is eluted, the column must be cleaned, or stripped, of all other materials. Once this is completed the resin is ready for reuse.

Slide 16. Ion Exchange Separation

If we were to measure the concentration of each radionuclide in the resin eluent as a function of time or volume, we could determine the effectiveness of separation of one radionuclide from the other.

The graph shown on the left of this slide displays a clean baseline separation of two components. The figure on the right shows a separation that is incomplete and there is an overlap of the two components in the eluent.

Slide 17. Key Factors for Good Ion Exchange Separation

The important technical concepts to be remembered for this section are that:

- Proper initial column preparation is important. The beads should always remain hydrated, and pretreated with a solution isotonic to the sample solution before sample introduction.

- Flow rate through the resin must be controlled so that effective diffusion into and out of the ion exchange beads can occur.
- Introduction of the analyte to the resin should be done in as small a sample volume as possible to minimize band spreading.

Slide 18. Choice of Elution Conditions: Effect of pH

The equation shown on the slide represents a simple example of an ion exchange equilibrium. It is easy to see that the concentration of H^+ ion can significantly affect the position of this equilibrium. This is just one of the solution parameters that must be considered when performing ion exchange separations.

Slide 19. Choice of Elution Conditions: Complexation by Ligands

In the previous module where we discussed complexation we saw that certain ligands can transform the ionic identity of a metal ion from a cation to an anion. The specific examples were any metal ion with a charge of +3 or less becomes an anion when paired with one molecule of EDTA. In the analysis of milk for strontium-90, the milk sample is passed over a cation exchange resin and all the calcium, strontium and barium are removed as cations. However by adjusting the pH to 4.5 to 5.5 and adding EDTA as an eluent, the calcium is complexed forming an anion that is no longer retained by the cation resin. At that pH the strontium and barium are unaffected by EDTA and remain as cations on the column. In this manner we selectively remove a non-radioactive, yield contaminant in the analysis calcium.

Slide 20. Ion Exchange: Capacity

Capacity of a resin is defined as the number of milli-equivalents per gram that a resin can remove before it breaks through and is no longer effective at ion removal. The ranges are shown on the slide. Since the ions that are removed generally have lower molecular weights than the ions that replace them it is fair to say that the resins actually “gain weight” in this process. The number of sites that are used by the contaminant depends on its ionic charge, so half as many +2 ions would be removed as +1 ions. As a specific example only half as many radium ions would be removed from a solution as there are hydrogen ions on the resin to start with.

Slide 21. Test Yourself Exercise #2

For each of the analytes shown calculate the total mass that could possibly be removed from a solution that comes in contact with 10 mL of a resin that has a cation capacity of 1.65 meq/mL. Click on the box to the right for a hint to help solve this problem.

Slide 22. Test Yourself Exercise #2 Solution

Review the answers shown on this slide and compare to the results that you obtained.

Slide 23. Capacity versus Mass

For each ion in the previous example the exact same number of equivalents is removed, but because their equivalent weights are so varied (because of their charge) the mass removed is different in each case.

Slide 24. Conclusion

Now that we have completed this module you should be able to:

- Describe the ion exchange process and the chemical environments that can affect the selectivity of an individual ion.
- Calculate the total capacity of a resin bed and determine if the sample contaminants will exhaust the capacity of the resin or allow it to freely exchange ionic materials from solution.
- Discuss the order of selectivity of ions based on charge and charge density.
- Discuss how to load a radionuclide onto an ion exchange resin and how to selectively elute a specific radionuclide.